Tests showed that males are more attracted to virgin females in the black perforated cages than to those in the transparent non-perforated cage (Fig. 1). This finding suggests that compounds released by females are responsible for the attraction of males. It has also been shown that the visual effect appeared not to play an important role in the attraction of males.

Figure 2 shows that the attraction of males to the white cage without females was due to a positive phototaxis shown by these insects.

Chemical analyses of the hexane extract of virgin female *B. pomorum*, by GC and GC-MS, revealed that it is mainly composed of a mixture of straight- and branched-chain hydrocarbons (C_{25}–C_{30}) and the two esters, hexadecyl 2-ethylhexanoate and octadecyl 2-ethylhexanoate (Fig. 3). In ethological tests carried out in the laboratory with virgin male *B. pomorum*, the hexane extract proved to be active. Males displayed courtship behaviour (antennation, lateral bouncing and wing vibrations) in the presence of a filter paper impregnated with hexane extract. In addition, electrophysiological studies, performed with live virgin males, have shown that male antennae give a positive response to hexane extracts of virgin females. These findings strongly suggest that female *B. pomorum* produce an attractant which enable males to find them.

References

1. Medina-Gaud, S., Bennett, F. D., Segarra-Carmona, A. E. & Pantoja, A., Notes on insect pests of soursop (guanábana), *Annona muricata* L., and their natural enemies in Puerto Rico. *J. Agric. U. Puerto Rico*, **73** (1989) 383–90.
2. Nadel, H. & Peña, J. E. Seasonal oviposition and emergence activity of *Bephratelloides cubensis* (Hymenoptera: Eurytomidae), a pest of *Annona* species in Florida. *Environ. Entomol.*, **20** (1991) 1053–7.
3. Peña, J. E., Glen, H. & Baranowski, R. M. Important insect pests of *Annona* spp. in Florida. *Proc. Fla. State Hort. Soc.*, **97** (1984) 337–40.
4. Vinson, S. B., Courtship behaviour and source of a sexual pheromone from *Cardiochiles nigriceps* (Hymenoptera; Braconidae). *J. Entomol. Soc. Amer.*, **71** (1978) 832–7.
5. Weseloh, R. M., Dufour's gland: source of sex pheromone in a hymenopterous parasitoid. *Science* (*Washington*), **193** (1976) 695–6.

Influence of Formulants and Salt Formation on Volatilisation and Activity of Pyrimethanil

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Abstract: Pyrimethanil is an anilinopyrimidine fungicide which is highly effective against grey mould (*Botrytis cinerea*) in many crops. Some of its effectiveness can be attributed to localised vapour-phase activity in parts of the canopy not reached by foliar spray. Control of pyrimethanil volatilisation was investigated using matrix-forming materials or by formation of salts using organic acids. Whilst matrix formation had little effect, organic salts of pyrimethanil showed much reduced volatility. Some of the salts showed different biological potential against cereal pathogens that were not well controlled by parent pyrimethanil. In addition, salt formation offered the possibility of significant changes to the physical form of pyrimethanil, opening up new formulation and co-formulation opportunities.

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Key words: pyrimethanil; volatility; matrix; salts; formulation

1 Introduction

The anilinopyrimidine fungicide, pyrimethanil, offers highly effective control of grey mould (*Botrytis cinerea* Pers. ex Fr.) in a variety of crops.[1] Some of the activity can be attributed to vapour-phase effects, as the compound has a vapour pressure of 2·2 mPa, and, as the molecule is readily metabolised, such external redistribution can offer protection to new growth.

It was postulated that control of vapour release may increase the window of activity, and may give enhanced activity against pathogens against which this molecule is less effective. For example, activity against cereal pathogens is minimal, this being largely attributed to rapid metabolism subsequent to foliar penetration. Maintaining a surface matrix for controlled release and minimised penetration might prolong activity, particularly since studies by other workers have shown that it is possible to reduce the rate of vapour release of chlorpyrifos by using matrix-forming materials in controlled-release emulsions.[2]

2 Materials and methods

In order to evaluate the influence of matrix-forming materials on volatility, a range of esters was selected for evaluation for this purpose, including cetyl palmitate, stearyl palmitate, distearyl phthalate, pentaerythritol tetrastearate, myristyl myristate, synthetic spermaceti, sorbitan monopalmitate and PEG600 distearate. Their melting points range from 38 to 61°C. Abietic acid was also evaluated.

In addition to evaluating such matrix-forming materials, a selection of air-polymerising linseed oil derivatives of varying viscosity was also evaluated. As with the matrix-forming materials, the linseed oils were evaluated at 0·5, 1·0 and 2·0 g litre^{-1}. Pyrimethanil was used at 0·5 g litre^{-1} in all treatments. The various treatments were made up in toluene solution; pyrimethanil was co-dissolved with the various matrix materials or oils and [^{14}C] pyrimethanil was used to facilitate monitoring of loss. All treatment solutions were applied to glass cover slips which were randomly positioned in a controlled-environment room. Up to five replicates per

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treatment were used. At selected time intervals, cover slips were removed from the chamber and placed in vials containing cocktail prior to liquid scintillation counting.

Initial investigations indicated that abietic acid reduced volatility by salt formation rather than due to a true release-matrix effect. The simple fatty acids: acetic acid, lauric acid, myristic acid, palmitic acid, stearic acid and oleic acid were therefore investigated. These were co-dissolved with pyrimethanil at 1:1 and 1:2 molar ratios of pyrimethanil: acid, the pyrimethanil being maintained at 0·5 g litre^{-1}.

In addition to the fatty acids which were investigated for volatility redution, a large range of other organic acids were used to make pyrimethanil salts. These were isolated, characterised and formulated as simple WP formulations for biological evaluation against a range of pathogens.

3 Results and discussion

Volatility. As alluded to in the preceding section, matrix-forming materials, when used at commercially acceptable rates (for one-pack products), had minimal long-term impact on the volatilisation of pyrimethanil. However, salt formation with the high-melting-point abietic acid indicated salt formation to be a viable approach. Some salts with fatty acids showed considerable potential to reduce loss due to volatility (Table 1). Predictably, the use of acetic acid had no impact on volatility, as the resultant salt did not differ greatly in molecular weight from pyrimethanil, but salts with the longer-chain acids showed massive reduction in volatilisation of pyrimethanil.

Biological activity. A range of organic salts were investigated, both by treating the salt as a new active ingredient and by adjusting doses to pyrimethanil-equivalence. Activity benefits were demonstrated in both cases.

When tested against *Erysiphe graminis* DC on wheat using a standard seven-day protectant protocol, the pyrimethanil 2*H*-1-benzopyran-3-carboxylate salt (50 g kg^{-1} WP formulation) showed nearly 80% disease control at 100 g per salt compared with less than 30% control by the corresponding pyrimethanil 50 g kg^{-1} WP. Similarly, in a 21-day protectant test against *Leptosphaeria nodorum* Muell., both this salt and a 50 g kg^{-1} WP of dipyrimethanil phthalate showed two-fold greater activity at the same dose.

TABLE 1
Surface Recovery of [^{14}C]-Pyrimethanil 2 h after Application to a Glass Surface in Combination with Fatty Acids at a 1:1 Molar Ratio

Fatty acid	*Recovery (% of radioactivity applied)*
None	3·1
Oleic	77·9
Lauric	66·9
Myristic	71·9
Palmitic	61·9

4 Conclusions

It has been shown that formation of organic salts of pyrimethanil greatly reduces its potential loss by volatilisation. In addition, increased activity against a selection of pathogens has been achieved which may be related to reduced loss. However, differing physicochemical properties of the salts could also influence their 'availability' to the required target site, and may also be a hindrance to formulation. For example, if the organic acid is too water-soluble, an SC formulation is not viable. In addition, the salt of such an acid (e.g. saccharin) can rapidly decompose upon addition of a dry formulation to the spray tank, resulting in such physical problems as flocculation and mixing incompatibility. However, in the case of lipophilic ion-pairs, advantages have been gained. For example, the oleate salt is a low-viscosity liquid which is readily emulsifiable, offering new formulation opportunities in EC, EW and SE formulations and co-formulations. Similar advantages have been noted for a new ester of fluroxypyr.[3]

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References

1. Neumann, G. L. & Winter, E. H., Pyrimethanil: a new fungicide. *Proc. Brighton Crop Prot. Conf. Pests Dis.* (1992) 395–402.
2. Chen, J. L., Horne, P. A., Jackson, W. R., Lichti, G. & Park, D., Volatility control for foliage-applied chlorpyrifos by using controlled release emulsions. *J. Controlled Release*, **29** (1994) 83–95.
3. Snel, M., Banks, G., Mulqueen, P. J., Davies, J. & Patterson, E. A., Fluroxypyr butoxy-1-methyl ester; new formulation opportunities. *Brighton Crop Prot. Conf. Weeds* (1995) 27–33.

Inhibitors of Appressorium Formation in *Magnaporthe grisea*: a New Approach to Control Rice Blast Disease

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